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Emission mechanisms of titanium oxide ions during sputtering

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By cesiating an oxygenated titanium surface, the work-function dependence of the sputtered atomic and oxide-ion yields during 500-eV Ne^+ bombardment were measured. The experimental data indicate that the negative titanium oxide ions are formed mostly by the fragmentation of the surface lattice while the positive oxide ions, especially at low oxygen coverages, are probably formed primarily by the recombination of the sputtered atomic ions and neutrals.

There are two models for the emission of molecular species during sputtering. The fragmentation model[1] assumes that the molecular species are emitted as complete fragments of the surface lattice during ion bombardment. The recombination model[2,3] assumes that only atomic species are emitted and that molecules are formed through the attractive interaction between neighboring sputtered atoms during the same sputtering event. There are many pieces of evidence that seem to support one of the models exclusively. These include experiments on sputtering yields,[4,5] angular distributions,[6] and energy distributions.[2] Details are contained in two recent reviews[7,8] of the subject. With very few exceptions,[9] the effects of the charge state of the molecular species are usually not discussed in spite of the fact that a majority of the empirical data came from secondary-ion mass-spectrometry experiments. No theory has yet suggested that the charge state and the formation mechanism are connected. This Communication reports the first experimental indication that both emission mechanisms can exist simultaneously on the same target surface and that the emission mechanisms can be different for different charge states of a sputtered molecular species. We have found that, during the bombardment of a cesiated-oxygenated titanium surface by Ne^+, negative titanium oxide ions are probably emitted by the fragmentation of the surface lattice while the formation of positive titanium oxide ions are consistent with the recombination mechanism, especially at low oxygen coverages.

The key idea of this experiment was that, if these oxide ions are emitted by the recombination processes, their ionization probabilities should show a predictable correlation with those of Ti and O. On the other hand, the ionization probabilites of different molecular species formed directly by fragmentation would depend on their individual ionization potential, or electron affinity, and matrix element of the electronic transition.[10] It is well known that the presence of Cs can change the ionization probabilities of both positive and negative secondary ions.[11] Hence by depositing controlled amounts of Cs on the target surface, we can use the ionization probabilities of Ti and O and ions as parameters to test the recombination concept.

The experiment was performed in an ultrahigh-vacuum system with a base pressure about 2×10^{-10} Torr. The Ti sample was a 25-μm-thick MARZ grade polycrystalline foil. The surface cleaning procedure consisted of repeated cycles of heating and 500-eV Ne^+ bombardment with *in situ* Auger electron analysis. The Ti surface was then exposed to 3 to 12 L (1 L $= 10^{-6}$ Torr sec) of O_2 at room temperature. The amount of adsorbed oxygen was characterized by the ratio (Auger ratio) of the 510-eV oxygen Auger peak to 418-eV Ti Auger peak. Cs was applied to the sample surface by thermal evaporation from a throughly outgassed Cs getter (SAES Getters). The electron-beam retarding-field method[12] was used to measure the work-function change $\Delta\phi$ to an accuracy of about ± 0.05 eV. It has been established that, for many systems, it takes about $\frac{1}{4}$ of a monolayer of Cs to obtain the maximum lowering of the work function.[13] The effect of Cs on the total sputtering yields should be a second-order effect. This assumption is supported by an experiment where the much lighter and smaller Li atoms were used to induce the lowering of the work function. No qualitative difference from the Cs case was observed except that Li induces a smaller $\Delta\phi$. A differentially pumped ion gun provided a 1-nA, 3-mm-diam, Ne^+ beam at 45° of incidence for sputtering in a static mode[1] condition. The secondary ions were detected with a quadrupole mass spectrometer equipped with a 0.5-eV-pass-width energy analyzer. The mass spectrometer axis was at 45° with the sample normal. The ion energy distributions (IED) of the secondary ions were scanned and the ion yields were integrated from 0 to 30 eV for the O^-, Ti^+, and TiO^+ ions and between the 10% points of the IED's ($\sim$10-eV width) for the less abundant TiO^-, $TiO_2^\pm$, $TiO_3^\pm$ ions.

In the recombination model, TiO^+ can result from the recombination of Ti^+ and O^0, Ti^0 and O^+, Ti^- and

O^{2+}, or other Ti and O combinations with a net charge of +1. However, the emission of Ti^+ is intense while the formation of Ti^- is negligible owing to its very small electron affinity (0.2 eV). Also, the emission of O^+ and other multiply charged ions is small and can be neglected. The $Y(O^-)/Y(O^+)$ yield ratio measured was about 50 in the absence of Cs and increased very rapidly with Cs coverage. Hence only the recombination of Ti^+ and O^0 is important. The probability of the emission of TiO^+ is then related to that for Ti^+ and O^0 by the following:

$$p(\mathrm{TiO}^+,E,\Delta\phi) = \sum_{E_1,E_2} p(\mathrm{Ti}^+,E_1,\Delta\phi)p(\mathrm{O}^0,E_2,\Delta\phi) \quad . \tag{1}$$

Here the summation is over all the possible energy combinations (E_1,E_2) which can yield a stable TiO^+ with emission energy E. Empirically the IED's of Ti^+ and O^- showed relatively little change with Cs coverage in spite of the large change in the ionization probabilities. Its immediate consequence is that the work-function dependencies of the emission probabilities can be factored out in the first approximation:

$$\begin{aligned} p(\mathrm{Ti}^+,E,\Delta\phi) &= r(\Delta\phi)p(\mathrm{Ti}^+,E,0) \quad , \\ p(\mathrm{O}^-,E,\Delta\phi) &= t(\Delta\phi)p(\mathrm{O}^-,E,0) \quad . \end{aligned} \tag{2}$$

Since Ti^0 and Ti^+ formed practically all the sputtered Ti atoms whose total yield was essentially independent of $\Delta\phi$, the $\Delta\phi$ dependence of $p(Ti^0)$ can also be factored out in the first approximation. A similar argument holds for $p(O^0)$. Hence,

$$\begin{aligned} p(\mathrm{Ti}^0,E,\Delta\phi) &= s(\Delta\phi)p(\mathrm{Ti}^0,E,0) \quad , \\ p(\mathrm{O}^0,E,\Delta\phi) &= u(\Delta\phi)p(\mathrm{O}^0,E,0) \quad . \end{aligned} \tag{3}$$

By definition, for $\Delta\phi=0$, $r(0)=s(0)=t(0)=u(0)=1$. By applying these results to Eq. (1) and similar equations for other oxide ions, these relations for the ion energy integrated positive-ion yields are obtained

$$\begin{aligned} Y(\mathrm{Ti}^+,\Delta\phi) &= r(\Delta\phi)Y(\mathrm{Ti}^+,0) \quad , \\ T(\mathrm{TiO}^+,\Delta\phi) &= r(\Delta\phi)u(\Delta\phi)Y(\mathrm{TiO}^+,0) \quad , \\ Y(\mathrm{TiO_2}^+,\Delta\phi) &= r(\Delta\phi)u^2(\Delta\phi)Y(\mathrm{TiO_2}^+,0) \quad , \\ Y(\mathrm{TiO_3}^+,\Delta\phi) &= r(\Delta\phi)u^3(\Delta\phi)Y(\mathrm{TiO_3}^+,0) \quad . \end{aligned} \tag{4}$$

With $r(\Delta\phi)$ measured in the experiment on atomic Ti^+, Eqs. (4) offer three independent determinations of $u(\Delta\phi)$. The test of the recombination model is based on whether these u values (u_1, u_2, u_3, respec-

TABLE I. Values of u_1, u_2, and u_3 for TiO^+, TiO_2^+, and TiO_3^+ calculated from Eq. (4), respectively. If the recombination model is correct, $u_1=u_2=u_3$. (NA represents not available due to insufficient signal.)

Auger ratio [O]/[Ti]	$-\Delta\phi$ (eV)	TiO^+ u_1	TiO_2^+ u_2	TiO_3^+ u_3
0.65	0	1	1	NA
	0.40	1.0	1.0	
	0.65	0.9	0.95	
	0.91	1.3	1.1	
	1.24	1.6	1.1	
0.84	0	1	1	NA
	0.96	0.82	0.90	
	1.79	0.92	0.96	
	2.09	1.1	1.2	
1.0	0	1	1	NA
	0.95	0.76	0.92	
	1.49	0.65	0.92	
	1.96	0.68	1.0	
	2.38	0.71	1.0	
	2.61	0.75	1.0	
1.24	0	1	1	1
	0.81	0.60	0.79	1.1
	1.13	0.53	0.75	1.1
	1.40	0.48	0.71	1.1
	1.83	0.46	0.72	0.97
	2.48	0.46	0.70	1.2
	2.90	0.47	0.84	1.2

tively) are self-consistent and physically acceptable.

The positive oxide ions show good agreement with the predictions of the recombination mechanism. All positive-ion yields are suppressed by the decrease in the work function due to the Cs coverage. It is interesting to note that the dependencies of the ion yields on $\Delta\phi$ are not exponential. Table I shows the values of $u(\Delta\phi)$ for different oxygen coverages, with u_1, u_2, and u_3 determined independently from Eq. (4) using the TiO^+, TiO_2^+, and TiO_3^+ yields, respectively. The range of $\Delta\phi$ was larger for higher oxygen coverages because of the larger oxide-ion signals and the larger initial work-function increase (~ 1 eV) owing to the oxygen adsorption. For low oxygen coverages where the Auger ratio ([O]/[Ti]) equaled 0.64 and 0.84, the averaged u_1/u_2 ratio for the data presented in Table I is 1.05 ± 0.18 ($\Delta\phi = 0$ cases excluded). The data covered over one and $\frac{1}{2}$ orders of magnitude change in the Ti^+ yield. This is in good agreement with the expectation of the recombination model where u_1/u_2 should be equal to unity. Another interesting observation is that all u values remained very close to unity in spite of the large $\Delta\phi$ changes which caused the O^- yield to increase by one and $\frac{1}{2}$ orders of magnitude. This implies that the O^- ions always remained a minority at all Cs coverages and the sputtered oxygen atoms were mostly neutral.

At higher oxygen coverages, there were systematic deviations from this good agreement. When the Auger ratio $[O]/[Ti] \simeq 1.0$, there was a definite drop in u_1 after the introduction of Cs, but u_1 remained fairly constant at higher Cs coverages while u_2 stayed close to unity. A possible cause of the residual differences between the values of u_1 and u_2 is that TiO^+ is formed by both fragmentation and recombination. The deviation from the recombination model was even greater at higher oxygen coverage where the Auger ratio $[O]/[Ti] = 1.24$. Figure 1 shows this high oxygen coverage case where all three oxide-ion yields had sufficient amplitude to be studied. Both u_1 and u_2 decreased rapidly from unity with the introduction of Cs: u_1 dropped even further than in the previous case. Nevertheless, the u_3 values determined from the TiO_3^+ yields were close to unity. Again a plausible cause of this phenomenon is that the higher oxygen coverage promoted the formation of TiO^+ and TiO_2^+ by fragmentation.

However, for the negative ions, the experimental

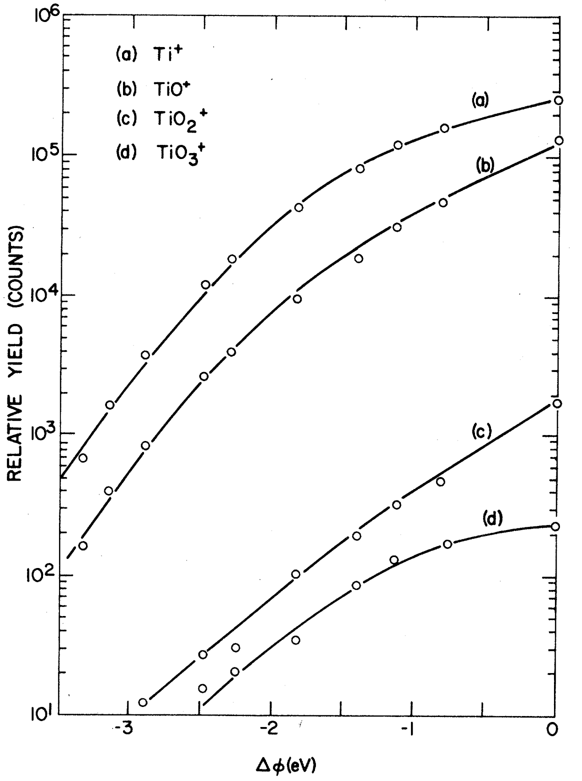

FIG. 1. Work-function dependence of the yield of Ti^+, TiO^+, TiO_2^+, and TiO_3^+ at high oxygen coverage. The Auger ratio for [O]/[Ti] is 1.24 (see text). The primary ion was 500-eV Ne^+.

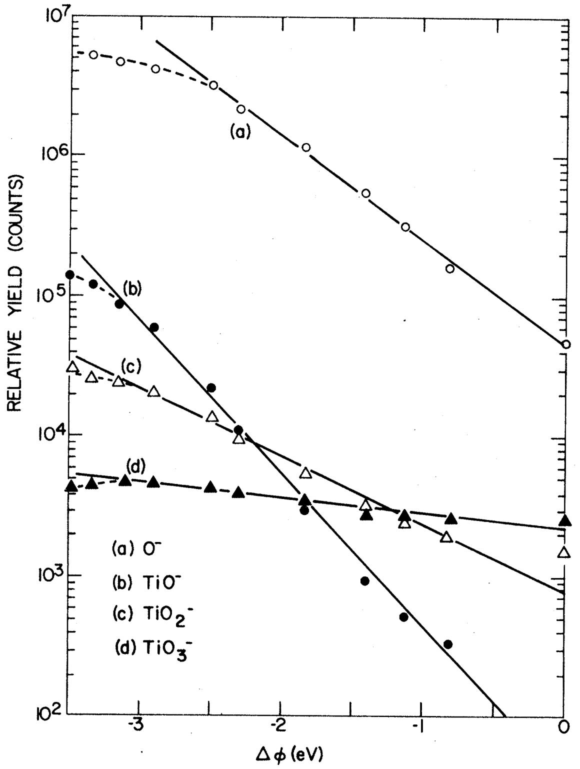

FIG. 2. Work-function dependence of the yield of O^-, TiO^-, TiO_2^-, and TiO_3^- at high oxygen coverage. The Auger ratio for [O]/[Ti] is 1.24 (see text). The exponential behavior was similar at all other oxygen coverages. The primary ion was 500-eV Ne^+.

data fail to fit the recombination model. Hence the negative titanium oxide ions were most probably formed by the fragmentation of the surface lattice. Figure 2 shows the work-function dependence of the O^-, TiO^-, TiO_2^-, and TiO_3^- yields for Auger ratio $[O]/[Ti] \simeq 1.24$. It was consistently observed at all oxygen coverages that empirically the negative-ion yields vary exponentially with $\Delta\phi$:

$$Y^- \propto \exp(-\Delta\phi/\epsilon_0) \quad . \tag{5}$$

Here ϵ_0 (in eV) was 0.54 ± 0.02, 0.38 ± 0.02, 0.78 ± 0.06, and 3.7 ± 0.3 for O^-, TiO^-, TiO_2^-, and TiO_3^-, respectively. The ion yields deviated from Eq. (5) when ϕ was close to the work-function minimum. There was little difference between 500- and 3000-eV Ne^+ bombardment. Such behavior has previously been observed for many other negative atomic ions[14] with ϵ_0 related to the electron tunneling parameters. Incidentally, that different molecular species have different ϵ_0 values eliminates the possibility that the exponential dependencies of $\Delta\phi$ are of thermal origin.[11]

If the recombination mechanism were correct for the negative oxide ions, it would give the following relations for the negative ions yields:

$$\begin{aligned} &Y(O^-,\Delta\phi) = t(\Delta\phi)\,Y(O^-,0) \quad , \\ &Y(TiO^-,\Delta\phi) = s(\Delta\phi)t(\Delta\phi)\,Y(TiO^-,0) \quad , \\ &Y(TiO_2^-,\Delta\phi) = s(\Delta\phi)t(\Delta\phi)u(\Delta\phi)\,Y(TiO_2^-,0) \quad , \\ &Y(TiO_3^-,\Delta\phi) = s(\Delta\phi)t(\Delta\phi)u^2(\Delta\phi)\,Y(TiO_3^-,0) \quad . \end{aligned} \tag{6}$$

Interpretation of the experimental data by Eqs. (6) would imply that both $s(\Delta\phi)$ and $u(\Delta\phi)$, and hence the probabilities of the emission of a neutral Ti atom and a neutral oxygen atom, respectively, depend exponentially on $\Delta\phi$. This is physically unlikely and in complete disparity with the positive-ion yield result that $u(\Delta\phi) \simeq 1$. With the failure of the recombination model, the negative oxide ions are most likely formed by the fragmentation of the surface lattice.

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